

# Polycyclic aromatic hydrocarbons in residential air of ten Chicago area homes: Concentrations and influencing factors

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## Abstract

Indoor and outdoor air samples at 10 non-smoker homes in the Chicago area were concurrently collected once per month for a 14-month period starting June 2000. During each sampling event, temperature, humidity, CO<sub>2</sub>, and CO were recorded. Questionnaires were used to register household activities. For each sample, 16 polycyclic aromatic hydrocarbons (PAHs) were measured using gas chromatograph and mass spectrometer (GC/MS). The total concentration of the 16 PAHs ( $\Sigma$ PAHs) ranged from 13 to 2454 ng m<sup>-3</sup> in the indoor air and from 13 to 1865 ng m<sup>-3</sup> in the outdoor air. In most cases, the concentrations were found to be log-normally distributed. The sum of PAHs with molecular mass  $\leq 202$  ( $\Sigma$ Light-PAHs, excluding naphthalene and anthracene) were found to behave differently than the sum of those with molecular mass  $\geq 228$  ( $\Sigma$ Heavy-PAHs). Variations among seasons were significant for indoor  $\Sigma$ Light-PAHs, and temperature was found to positively correlate with indoor  $\Sigma$ Light-PAHs for nine of the 10 homes. For  $\Sigma$ Heavy-PAHs, the outdoor concentrations were found to be significantly higher in the fall and winter seasons than in the summer. The correlations of indoor and outdoor concentrations appear to be weak for light PAHs, but reasonably strong for heavy PAHs. The medians of indoor-to-outdoor ratio (I/O) are less than or very close to 1 for all PAHs except anthracene. The indoor concentrations of  $\Sigma$ PAHs tend to be higher as the age of the houses increases, and the surrounding industrial pollution was found to have impact on outdoor  $\Sigma$ Heavy-PAHs. For light PAHs indoors, comparison among homes indicates that the impact of house characteristics and indoor activities tends to be greater than the influence of the penetrating outdoor air.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds that consist of two or more fused benzene

rings. They are the by-products of the incomplete combustion or pyrolysis of virtually all organic matter (Harvey, 1991). PAHs are considered the most widely distributed class of potent carcinogens present in the human environment, and many of them are listed as known, probable, or possible carcinogens by various international and national agencies. In addition to cancer, PAHs have also been found to cause morphological, physiological, and developmental abnormalities in test animals, increase allergic immune responses in

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human at low levels, and may act synergistically with other air toxics to cause adverse health effects (Harvey, 1997; Diaz-Sanchez et al., 1996; ATSDR, 1995).

Since most people spend more than half of their time at home, human exposure to PAHs in the indoor environment has received increasing attention in recent years (Ohura et al., 2004; Zhu and Wang, 2003; Naumova et al., 2002; Ohura et al., 2002; Chao et al., 2002; Levy et al., 2002; Van Winkle and Scheff, 2001; Liu et al., 2001; Koyano et al., 2001; Sugiyama et al., 2000; Wallace, 2000; Li and Ro, 1999; Prince et al., 1999; Sheldon et al., 1993, 1992; Chuang et al., 1991; Otson et al., 1991; Dubowsky et al., 1999; US Environmental Protection Agency, 1991). Studies conducted so far have shown that cigarette smoking is the predominant source of PAHs in homes with smokers; that indoor sources may exist for PAHs with 2- or 3-rings; and that outdoor air may contribute significantly to the indoor PAHs, especially those with 4 or more rings. In addition, indoor PAHs were found to be mostly associated with fine particles with diameters less than  $2.5\mu\text{m}$  (Koyano et al., 2001; Sugiyama et al., 2000), which are able to reach the lower respiratory tract in human body, thus substantiating the concerns about their effects on public health.

Although much has been learned, knowledge about the behavior of indoor PAHs is still very limited, due largely to the complex nature of the sources and the large number of potentially influencing factors. This research was initiated in 1999 with the overall objectives of assessing the levels of PAHs in urban non-smoker homes, evaluating the contribution of outdoor air to indoor PAH levels, and examining the factors that influence the PAHs concentrations in indoor air.

## 2. Methodology

### 2.1. Participating homes

A household screening questionnaire was used to select participants from all volunteers who responded to an advertising flyer. Homes with smokers were excluded to avoid the potential confounding effect from the more predominant source of cigarette smoke. Only single family homes were included. Consent forms, approved by the university's institutional review board (IRB Approval #1999-0605), were signed by each of the participants before sampling started. Six homes were located within Chicago city limits, three in near suburbs, and one in Gary, Indiana. The house styles include traditional two-story, ranch, and bungalows, with age ranging from 8 to 105 years. Six homes had gas forced air (GFA) heating systems, the others use radiator heating. For cooling, three homes had central air conditioning systems, four had window air conditioners,

and others had none. Only two homes had wood burning fireplaces but rarely used them during the study period. Seven homes used gas stove or oven, others used electric stoves. Only one had an attached garage.

### 2.2. Sampling

Air sampling was conducted from June 2000 to August 2001. Indoor and outdoor air samples were simultaneously collected once per month at each home. Indoor air samples were collected in the kitchen or in close proximity to the kitchen. This sampling location was selected because, in most homes in the Chicago area, the kitchen has more or is closer to potential PAH sources than other rooms and is often where most family activities occur. Outdoor air samples were simultaneously collected at locations no farther than 10 m from the house.

The procedure of sampling was developed based on the one described by Chuang et al. (1988). An AIR-CON-2 high volume air sampler (Gilian Instrument Corp., Caldwell, NJ) was used for outdoor sampling, and a Model AirChek HV30 pump (SKC, Eighty Four, PA), which produces little noise, was used for most indoor sampling events. A rotameter was calibrated using a bubble airflow meter in the lab and was used for field calibration of the pumps and sampling flow rate determination. Sampling time was 46–48 h and generally ran from morning to morning. For both pumps, the airflow rate was set at 10 L per min, resulting in a total air volume of approximately  $28\text{ m}^3$ . The air volumes actually collected were specific for recorded sampling time and converted to standard conditions ( $25^\circ\text{C}$  and 1.0 atm) in calculating PAH concentrations. The air was drawn by the pump through a filter-cartridge assembly. The filter was 3.2 cm diameter and made of quartz; it was designed to trap aerosol and particulate forms of semivolatiles (Supelco, Bellefonte, PA). The cartridge was a modified ORBO-1000 cartridge (Supelco, Bellefonte, PA), and consists of a 2.2 cm od  $\times$  7.6 cm long glass tube containing 3 cm of polyurethane foam (PUF), approximately 2 g XAD2 resin, and another 3 cm PUF. Exactly  $2\mu\text{L}$  of a field surrogate solution containing deuterated PAHs (see below) was added to the cartridge using a syringe before the pump was started. The filter-cartridge assembly was held at a height of 5 feet, which represents the human adult breathing zone while standing. The inlet of the cartridge was kept away from objects such as walls and furniture, which might block or interfere with the airflow. A household status questionnaire was used to establish the conditions of the home and the surrounding activities at the time of sampling.

During each sampling event, real-time continuous measurements of  $\text{CO}_2$ , temperature, and relative humidity were carried out both indoors and outdoors using

Models 8550 and 8551 Q-Trak air quality monitors (TSI, St Paul, MN). Concentration of carbon monoxide (CO) was also recorded indoors. The Q-Traks were calibrated every two months according to the operational manual, with the use of TSI-supplied zero air and CO<sub>2</sub>- and CO-containing air with known concentrations. A sampling data collection sheet was also used to log the starting and ending air quality and meteorological conditions. It was found that the Q-Trak, designed for indoor air quality monitoring, did not work well outdoors and generated unreliable values of temperature and relative humidity on direct exposure to outdoor meteorological conditions. Therefore, outdoor temperature and humidity data were collected from the National Weather Service data for O'Hare Airport in Chicago.

### 2.3. Chemical analysis

Samples were analyzed for 16 PAHs including naphthalene (NaP), acenaphthylene (AcNP), acenaphthene (AcN), fluorene (Fl), phenanthrene (PhA), anthracene (An), fluoranthene (FlA), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chy), benzo[b]fluoranthene (BbFlA), benzo[k]fluoranthene (BkFlA), benzo[a]pyrene (BaP), indeno[123-cd]pyrene (IP), dibenz[a,h]anthracene (dBahA), and benzo[ghi]perylene (BgHiP).

Solutions of PAH mixture were purchased from Ultra Scientific (North Kingstown, RI). Internal standard solutions containing naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, and perylene-d<sub>12</sub> were also purchased from Ultra Scientific. Deuterated PAHs used for field surrogates (fluoranthene-d<sub>10</sub> and benzo[a]pyrene-d<sub>12</sub>) and analytical surrogates (fluorene-d<sub>10</sub>, pyrene-d<sub>10</sub>, and benzo[g,h,i]perylene-d<sub>12</sub>) were purchased from Cambridge Isotopes (Boston, MA). Solvents used in this study were purchased from Fisher Scientific (Fair Lawn, NJ). Dichloromethane and hexane were GC grade, and ethyl ether was pesticide grade. Silica gel (100–200 mesh, Davisil Grade 644) and anhydrous sodium sulfate were also purchased from Fisher Scientific.

The procedures of sample pretreatment and instrumental analysis were developed based on EPA Compendium Method TO-13A (USEPA, 1999). Before extraction, exactly 2 µL of an analytical surrogate solution was added to the cartridge. The filter and the cartridge were extracted together on Soxhlet extractors using 10% ethyl ether in hexane for 24 h, followed by another 24-h extraction using dichloromethane. The extracts were then combined. The volume of the extract was reduced in a Kuderna–Danish (K–D) concentrator to about 5 mL, then a gentle stream of nitrogen was used to reduce the volume to 2 mL. For cleanup, the sample was passed through a glass column (11 mm × 300 mm) packed with 10 g of activated silica-gel and about 10 g of anhydrous sodium sulfate. The column was eluted

sequentially with 40 mL hexane, 40 mL 10% ethyl ether in hexane, and 40 mL of dichloromethane. After discarding the first 15, 120 mL of eluent was collected and the volume was reduced by K–D concentrator to about 4 mL, then further reduced by nitrogen to 2 mL.

An Agilent Model 6890+GC coupled with Model 5973 MS was used for quantitative analysis. The GC/MS was equipped with a programmable temperature vaporizing (PTV) inlet and a HP MS-5 column (30 m × 250 µm id, film thickness 0.25 µm). An injection volume of 60 µL (3 injections of 20 µL each) was used for all the samples. Helium was the carrier gas. The MS was operated in SIM mode. Quantification was based on the sum of the primary and two secondary ions. Concentrations of PAHs were calculated using peak area ratios and a five-point calibration standard curve against the internal standard used for that group. More detailed instrument conditions are described in Norlock et al. (Norlock et al., 2002).

### 2.4. QA/QC

Field blank and laboratory blank samples were analyzed to determine potential contamination. Instrument solvent blanks were run to check the status of the analytical system. Detailed procedures and the results of determining the instrument detection limits (IDLs) and method detection limits (MDLs) can be found in Norlock et al. (2002). The detection limits are far below the levels commonly found in the samples. The total number of PAH concentration data generated from this work is 3527, among which 190 were under MDL. All of the analytes (16 PAHs and 5 surrogates) were spiked into blank solvent in replicates to verify the reliability of each of the analytical steps including extraction, concentration, and cleanup by silica-gel chromatography, as well as the performance of the whole procedure. The recoveries of the native and deuterated PAHs were in the range of 70–126%, and relative standard deviation for replicates ranged from 2% to 25%.

The USEPA Method TO-13A (USEPA, 1999) requires the use of two field surrogates (fluoranthene-d<sub>10</sub> and benzo[a]pyrene-d<sub>12</sub>) and two analytical surrogates (fluorene-d<sub>10</sub> and pyrene-d<sub>10</sub>) for every sample. We used all the required surrogates plus benzo[ghi]perylene-d<sub>12</sub> as an additional analytical surrogate to better monitor the behavior of heavier PAHs during sample pretreatment and instrumental analysis. The recoveries of the surrogates were used for the purpose of tracking the accuracy and bias during the sampling and laboratory work. Among the field surrogates, 80% of FlA-d<sub>10</sub> recoveries and 71% of BaP-d<sub>12</sub> recoveries fell into the acceptable range of 40–140%. For analytical surrogates, 83% of pyrene-d<sub>10</sub> recoveries and 65% of benzo[ghi]perylene-d<sub>12</sub> were within this range. Recoveries of fluorine-d<sub>10</sub> were not calculated because,

in many samples, a co-eluting peak made it impossible to integrate even with the character ions extracted. The identity of the interfering substances was not determined.

### 2.5. Data analysis

The SAS System for Windows Release 8.1 and the MS Excel Analysis Tool Pack were used for statistical data analyses. Because the sampling design emphasizes repeated measurement at each of the 10 selected homes, it is necessary to analyze the data with repeated measure statistical techniques. GLM was used instead of ANOVA because the sample sizes of the groups involved are often different. Variations among homes and seasons were examined. Both Duncan's multiple range test and the Scheffe's multiple comparison option were used with the repeated measures GLM to identify the pairs of homes or seasons which were significantly different at the 95% confidence level. In the cases where

the distributions of the data were uncertain and the sample sizes are not large, one-way nonparametric analysis (NPAR1WAY procedures of SAS) was also performed, and the Wilcoxon rank sums scores and the  $\chi^2$  were obtained.

## 3. Results and discussion

### 3.1. Concentrations

Boxplots of indoor and outdoor PAH concentrations are shown in Fig. 1. In drawing the boxplots, the lowest concentrations were set to  $0.001 \text{ ng m}^{-3}$ . In calculations of means and median, non-detected values are conservatively treated as zeros. This resulted in slightly underestimated means but the correct estimate of the median.

With the exclusion of naphthalene, the total concentrations of the 15 PAHs in indoor air ranges from 2 to

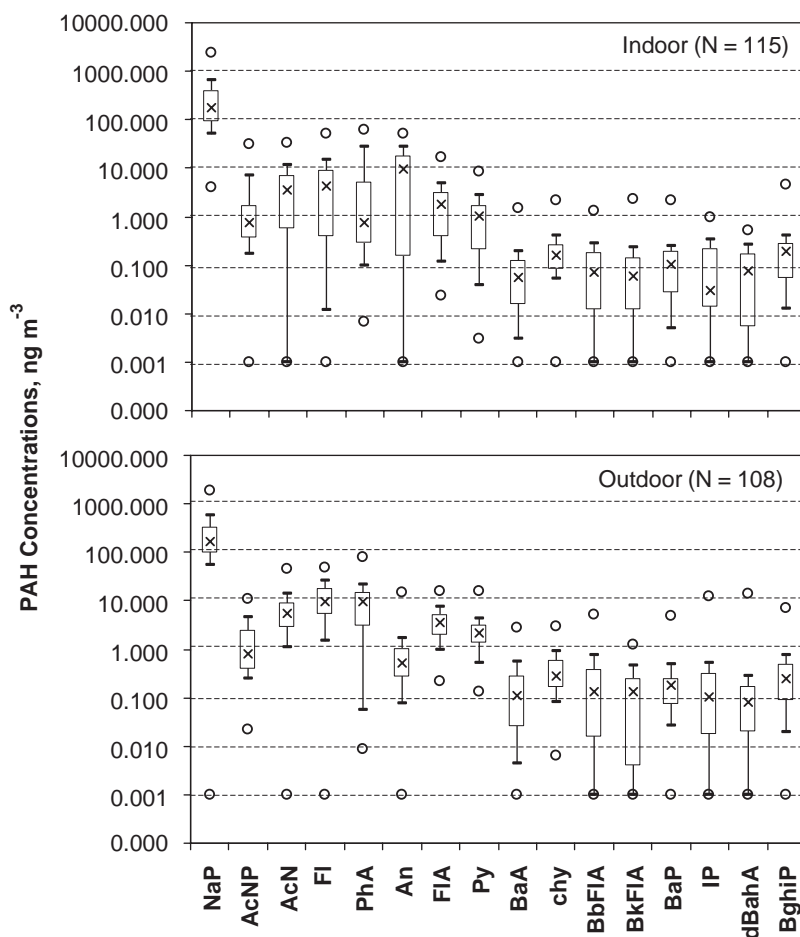


Fig. 1. Concentrations of individual PAHs in 10 Chicago homes. The  $\times$  is the median, the box represents 25–75% percentiles, the whiskers are 10% and 90% percentiles, and the circles are the minimum and maximum.

147 ng m<sup>-3</sup>, with an average of 36 ng m<sup>-3</sup> and a median of 30 ng m<sup>-3</sup>. The total outdoor concentration ranges from 4 to 180 ng m<sup>-3</sup>, with an average of 42 ng m<sup>-3</sup> and a median of 36 ng m<sup>-3</sup>. Statistical analysis found both indoor and outdoor total PAH concentration data, either with or without naphthalene, to be non-normally distributed based on the Shapiro-Wilk test for normality.

Naphthalene has the highest mean and median concentrations among the 16 PAHs (Fig. 1). The medians are 177 and 168 ng m<sup>-3</sup>, and the maxima are 2340 and 1867 ng m<sup>-3</sup>, for indoor air and outdoor air, respectively. Compared with two other indoor PAH studies in the US conducted in 1986 and 1994 (Chuang et al., 1991; Van Winkle and Scheff, 2001), indoor naphthalene concentrations found in this study are lower. Van Winkle and Scheff (2001) found that indoor naphthalene emission was largely associated with mothball usage, which, in turn, was found to be associated with variables of race (Hispanic) and location. In this study, only one home (Home 03) reported the use of mothball, but the naphthalene at this home is not higher than most other homes.

Following naphthalene, anthracene was found to be the second highest in indoor air, while fluoranthene and phenanthrene were the second highest in outdoor air with comparable means and medians (Fig. 1). All PAHs with molecular mass 152–202 have average concentrations higher than 1 ng m<sup>-3</sup> and their medians range from 0.5 to 19 ng m<sup>-3</sup>. By comparison, PAHs with molecular mass 228 or higher exist in air in significantly lower concentrations. No median or average for these heavy PAHs is above 0.25 ng m<sup>-3</sup> for indoor samples or 0.5 ng m<sup>-3</sup> for outdoor samples. The lower abundance of heavy PAHs relative to light PAHs has been reported in numerous studies (Ohura et al., 2004; Zhu and Wang, 2003; Naumova et al., 2002; Van Winkle and Scheff, 2001; Sheldon et al., 1993, 1992; Chuang et al., 1991).

### 3.2. Seasonal variations

To analyze the seasonal variations, the entire sampling period is arbitrarily divided into five seasons, including Summer1: June–August, 2000; Fall: September–November, 2000; Winter: December 2000–February, 2001; Spring: March–May, 2001; and Summer2: June–August, 2001. Data were analyzed on the basis of individual PAHs, grouped by the number of fused aromatic rings, and divided according to the molecular mass range. Most of the discussion below divides the PAHs into two groups: the sum of the six PAHs with molecular mass ≤202 (ΣLight-PAHs, excluding naphthalene and anthracene) and the sum of the eight PAHs with molecular mass ≥228 (ΣHeavy-PAHs). Naphthalene is excluded from ΣLight-PAHs, because of its predominance and the fact that it has an industrial

origin, while all other PAHs are solely from combustion sources. Anthracene was not included for the reasons discussed in the following section.

Fig. 2 compares the PAH levels among the five seasons. Indoor concentrations of ΣLight-PAHs differ significantly among the seasons, based on the repeated measure GLM ( $p < 0.0001$ ). On an individual basis, all the eight light PAHs, including naphthalene and anthracene, in indoor air have significant variations among seasons, resulting in a range of  $p$ -values from 0.0003 to 0.027. As shown in Fig. 2a (upper), higher concentrations of ΣLight-PAHs were observed in the two summers than in other seasons, although the difference between Summer2 and other individual seasons is not sufficiently large to be significant at the 95% confidence level. In addition, indoor ΣLight-PAHs was found to positively correlate with indoor temperature (48-h average during each sampling) in all the

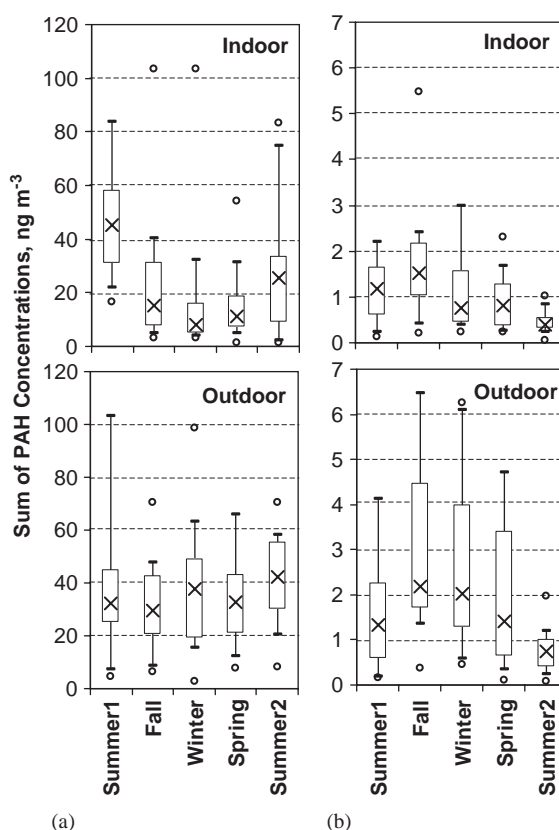


Fig. 2. Seasonal variation of PAH concentrations. (a) Sum of PAHs with molecular mass ≤202, excluding naphthalene and anthracene; (b) Sum of PAHs with molecular mass ≥252. The × is the median, the box represents the range between 25% and 75% percentiles, and the whiskers are 10% and 90% percentiles, and the circles are the minimum and maximum (the absence of a circle indicates the value is out of range of y-axis).



homes except Home-09, which is a much newer home, with the correlation coefficient  $R$  averaging 0.48 and ranging from 0.24 to 0.67. In contrast, the light PAHs outdoors did not vary significantly among seasons, as can be seen in Fig. 2a (lower) and evidenced by the high  $p$ -value of 0.54. During the cold seasons, the reduced PAH vaporization from surfaces with the decreasing temperature in the outdoor environment might be compensated by the higher emissions from increased fuel combustion for heating. The difference in indoor levels of  $\Sigma$ Light-PAHs between the two summers may be due to the difference in temperature, because the majority of the Summer1 samples were collected in July and August, while those of Summer2 were in June and July. The average indoor temperature recorded in Summer1 ranged from 25 °C to 32 °C. In Summer2, it ranged from 20 °C to 30 °C, with 30% of the time being below 25 °C and heavy overlap with the spring and fall temperature ranges.

The integrated Clausius–Clayperon equation is often used to explore the temperature dependence of organic chemicals in the gas phase (Schwarzenbach et al., 2003). For our PAH data, the power of this approach is weakened due to the facts that our concentration data do not separate gaseous from particulate PAHs, and that direct emissions of PAHs from numerous sources occurred during the sampling events, especially in the winter. Nevertheless, preliminary regression analyses, including the data from all 10 homes, on the natural log concentration of indoor  $\Sigma$ Light-PAHs ( $\text{ng m}^{-3}$ ) versus the inverse absolute temperature ( $\text{K}^{-1}$ ) result in negative slopes, as expected, for all seasons except winter. The temperature dependence of  $\Sigma$ Light-PAHs is relatively strong for the fall and both summers. By combining these three seasons, a slope of  $-12,700 \pm 3200 \text{ K}$  was obtained, with  $R^2 = 0.22$  ( $N = 58$ ). The positive slope for the winter,  $18,500 \pm 7500 \text{ K}$ , indicates the trend of increasing  $\Sigma$ Light-PAHs as temperature drops inside the houses ( $R^2 = 0.30$ ,  $N = 16$ ). This may result from increased combustion of natural gas and other fuels for warming. For the spring, such regression is very weak ( $R^2 < 0.01$ ,  $N = 28$ ), with a slope of  $-2800 \pm 6300 \text{ K}$ .

For  $\Sigma$ Heavy-PAHs, both mean and median of the Fall are the highest among all seasons both indoors and outdoors (Fig. 2b). In the study area, most homes closed windows and started the operation of heating appliances during this season. In addition to reduced air exchange with outdoors, it is possible that the start of GFA heating appliances re-suspended the particulate matter which had accumulated in the duct during non-heating seasons, resulting in dramatically enhanced PAH levels. Winter outdoor samples also had elevated levels of heavy PAHs, compared with the summers and the spring (Fig. 2b, lower). In addition, the medians of the ratio  $\Sigma$ Heavy-PAHs/ $\Sigma$ Light-PAHs for the fall and

winter are more than double those in the summers. Linear regression of outdoor  $\Sigma$ Heavy-PAHs versus inverse temperature gives positive slopes for both winter and spring, demonstrating the increasing levels of heavy PAHs in the air when temperature decreases. Elevated PAH levels in the urban atmosphere during winter have been reported for a number of cities in the northern hemisphere (Ohura et al., 2004; Guo et al., 2003; Ollivon et al., 2002; Park et al., 2001; Papageorgopoulou et al., 1999; Coleman et al., 1997; Viras and Siskos, 1993), and are often explained by the increase in fuel combustion for indoor heating. In winter 2000, the Chicago area experienced sequential heavy snowstorms and cold weather throughout the months of December and part of January. Natural gas consumption was high despite a skyrocketed energy price. Added to domestic heating is workplace heating at numerous businesses and industries in the area, which may have increased fossil fuel consumption in the winter.

Seasonal variation of urban atmospheric PAH concentration reflects the complexity of PAH sources. In an urban environment, traffic can be the primary source of atmospheric PAHs, and it is non-seasonal. In residential indoor environment, cooking as a source is non-seasonal, although outdoor barbecuing occurs mostly in summer and fall. Other non-seasonal sources, including candle and incense burning, chemical storage, and garage activities, can be strongly home-specific. Seasonal indoor combustion sources include fireplace wood burning and space heating using kerosene or natural gas, and both are winter events. In addition, indoor–outdoor air exchange can play an important role, and it is usually higher in the spring and fall (and summer in some homes that do not use air conditioning) due to window opening. It is also known that indoor semi-volatile organic compounds have a tendency to adsorb onto solid surfaces (Singer et al., 2003; Wilke et al., 2003; Van Loy et al., 1998), which then become secondary sources with their emission being strongly temperature dependent. Our results suggest, while light PAHs indoors largely depend on temperature and indoor activities, heavy PAHs outdoors are dominated by various emission sources, especially those outdoors.

### 3.3. Indoor vs. outdoor

To explore the relationship between indoor and outdoor PAHs, least square linear regression was performed on indoor concentration using outdoor concentration as the independent variable. The regression of the home median  $\Sigma$ PAHs (sum of all the 16 PAHs) resulted in a positive slope of 0.68 and an  $R^2$  of 0.27 ( $N = 10$ ). Regressions of  $\Sigma$ PAHs grouped by season resulted in positive slopes for all the seasons except Spring. However, the regression coefficient  $R^2$  values are low, showing that the dependence of indoor

concentration on outdoors is weak on the basis of  $\Sigma$ PAHs.

The correlations between indoor and outdoor concentrations were further analyzed for  $\Sigma$ Light-PAHs and  $\Sigma$ Heavy-PAHs, and the results are shown in Fig. 3. Apparently,  $\Sigma$ Light-PAHs, as well as individual PAHs with 2 or 3 rings with the exception of anthracene (see below), have substantial scattering on both sides of the  $y = x$  fit line. This suggests that either indoor or outdoor concentration can be higher than the other with comparable probability. On the other hand,  $\Sigma$ Heavy-PAHs and all individual heavy-PAHs tend to have higher concentrations outdoors regardless of the seasons. This finding agrees with a number of previous major studies on indoor PAHs (Ohura et al., 2004; Naumova et al., 2002; Van Winkle and Scheff, 2001; Chuang et al., 1991). It is likely that these heavier PAHs are mostly generated outdoors.

Fig. 4 shows the indoor-to-outdoor ratio (I/O) of individual PAHs. The median I/O observed in this study is less than or very close to unity for all PAHs except anthracene. The majority of I/O ratios of individual PAH compounds measured in our study are in the range of 0.5–1.0 and comparable to those measured by

Naumova et al. (2002). Sheldon et al. (1993, 1992) also reported that indoor air showed little or no increase in median or mean PAH concentrations compared to outdoor air. Mitra and Ray (1995) reported average I/O ratios ranging from 3.5 (benzo[ghi]perylene) to 14.8 (naphthalene) for eight non-smoker homes in Ohio during winters of 1986 and 1987 (Chuang et al., 1991); but the median values were not reported. In this work, a comparison of the median and the average indicates that the I/O values are highly skewed and non-normally distributed. Therefore, using averages for the I/O ratios of PAHs can be significantly misleading.

Indoor versus outdoor concentrations for all 16 individual PAHs as well as  $\Sigma$ Light-PAHs and  $\Sigma$ Heavy-PAHs were regressed for each home. For light PAHs, the 10-home average regression coefficient  $R^2$  ranges from 0.075 to 0.17, and the maximum ranges from 0.28 (acenaphthylene, Home 09) to 0.48 (fluorene, Home 10), showing no or very weak correlations between indoor and outdoor levels. By comparison, no average  $R^2$  is below 0.3 for all heavy PAHs except benzo[a]pyrene, for which average  $R^2 = 0.29$ . The highest  $R^2$  among the 10 homes ranges from 0.71 (benzo[b]fluoranthene, Home 02) to 0.97 (benzo[a]anthracene, Home 10). The stronger correlation between indoor and outdoor concentrations of heavy PAHs than light PAHs implies that the heavy PAHs found indoors may originate outdoors. It has been reported that the heavy PAHs are usually generated at higher temperatures, such as those in the diesel combustion engines, than those involved in most indoor combustion processes such as cooking and heating using natural gas (Nikolaou et al., 1984).

Anthracene stands out as the only compound with a clearly demonstrated indoor dominance. It has an unusually high I/O ratio of  $>10$  for 7 out of 10 homes and all seasons except summer. Although the possibility that an unknown compound interfered with the GC separation and MS identification of anthracene cannot be excluded, the large peak on the chromatograms of most indoor samples was confirmed by not only the retention time but also the ratio of the primary ion ( $m/z$  178) to the qualifier ions ( $m/z$  179 and 176). In most published PAH concentration profiles in ambient air, anthracene concentration is often lower than that of phenanthrene and many other PAHs such as pyrene. In our study, the same was observed for the outdoor air, but not for the indoor air. Anthracene is much more vulnerable than its isomer phenanthrene to radiations of near-ultraviolet and visible lights, due to its linear fused-ring structure (Schwarzenbach et al., 2003). Therefore, it is possible that anthracene in the outdoor air is subjected to more rapid degradation than the anthracene indoors where the intensity of light radiation is much lower. It is also likely that significant anthracene sources exist indoors. Indoor anthracene concentration may depend heavily on the home events and indoor activities,

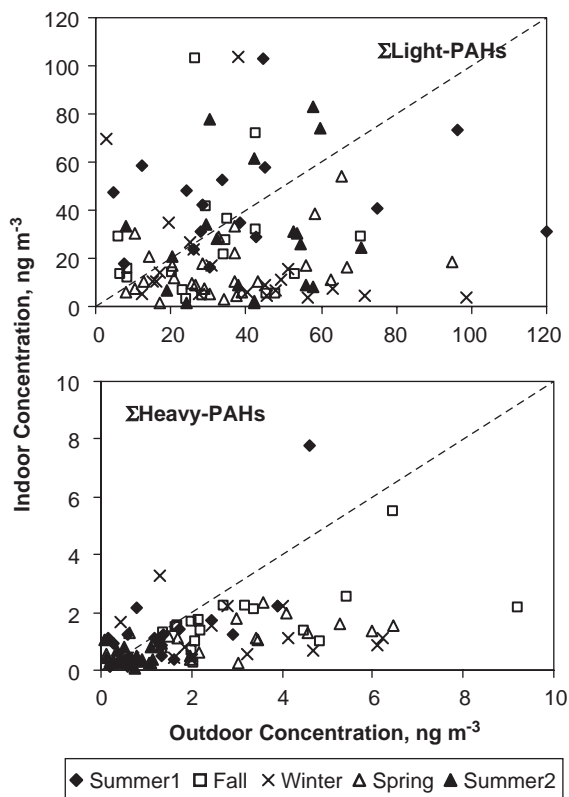


Fig. 3. Comparison of indoor and outdoor PAH concentrations. The dashed line is for  $y = x$  fit.

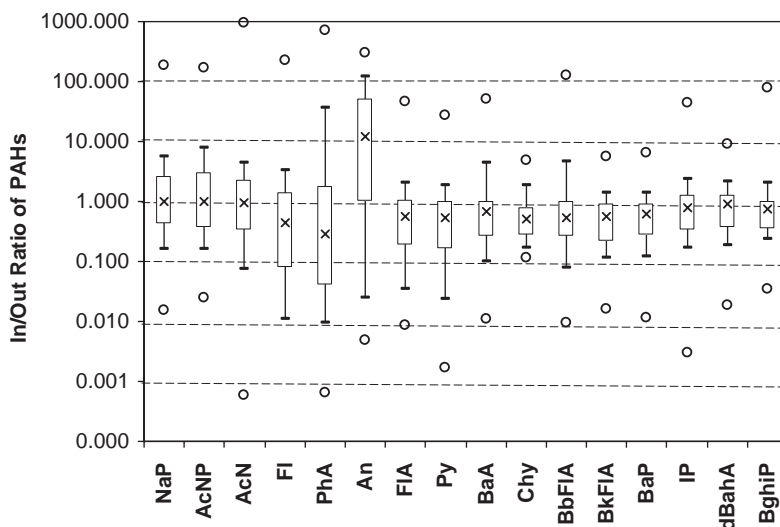


Fig. 4. Indoor-to-outdoor ratio of individual PAHs in 10 Chicago homes. The  $\times$  is the median, the box represents 25–75% percentiles, the whiskers are 10% and 90% percentiles, and the circles are the minimum and maximum.

because the I/O ratios vary widely across seasons and homes with a much higher standard deviation than other PAHs. To our knowledge, no previous studies have reported such dramatic differences in anthracene concentrations between indoors and outdoors. This observation warrants further investigation and confirmation.

### 3.4. Other influencing factors

The number of factors affecting PAH concentrations in the urban residential environment is large. A few potential factors are discussed below. In many cases, the limited number of observations weakened the power of statistical methods, thus discussion has to be based on direct comparisons. Therefore, caution is needed in generalizing the findings.

Age of the houses appears to positively affect the indoor PAH levels, as illustrated in Fig. 5 for  $\Sigma$ PAHs. As expected, there appears to be a tendency of having higher PAH levels indoors as the house gets older. More detailed analysis indicates that the dependence of home median concentration on house age is strong for naphthalene (slope = 2.5,  $R^2 = 0.48$ ), and weak for  $\Sigma$ Light-PAHs (slope = 0.10,  $R^2 = 0.15$ ) and  $\Sigma$ Heavy-PAHs (slope = 0.62,  $R^2 = 0.09$ ). Sorption on and re-emission from building materials such as carpet, wall-board, furniture, etc., of many chemicals released from cigarette smoking, including naphthalene and phenanthrene, have been reported (Singer et al., 2003; Wilke et al., 2003; Van Loy et al., 1998). Such sorption may not be completely reversible, thus the amount sorbed on various solid surfaces in homes

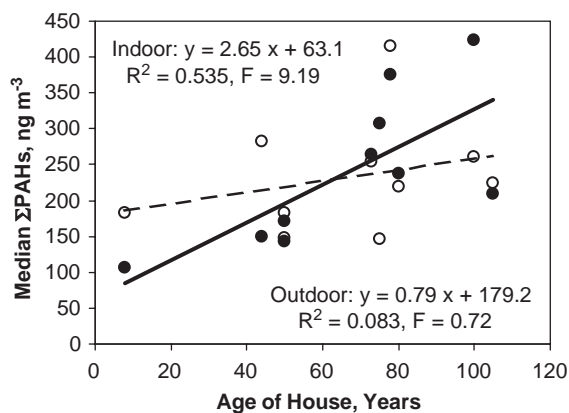


Fig. 5. Dependence of home median total PAH concentration on age of the houses. Indoor air—filled circles and solid line; outdoor air—empty circles and dashed line.

may accumulate over time. Compared with those indoors, the outdoor levels are much less influenced, although a positive slope was obtained for  $\Sigma$ PAHs (see Fig. 5). Due to the limited number of homes involved in this study, future work is needed to demonstrate and understand the long-term accumulation of PAHs and other semi-volatile organic compounds in indoor environment.

For light PAHs, comparison among homes suggests that the impact of house characteristics and indoor activities on the indoor level is greater than the influence of the penetrating outdoor air. For instance, Homes 09 and 10 were located in the same neighborhood, thus



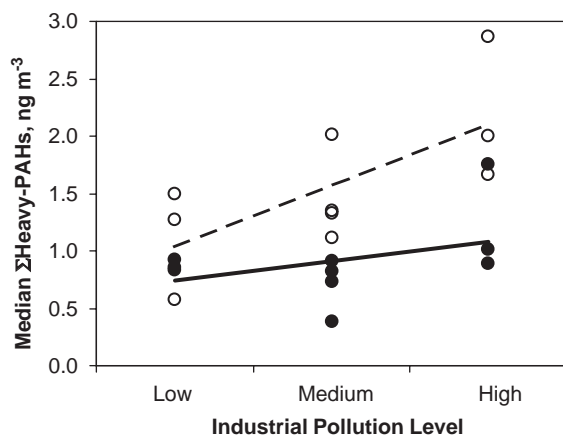


Fig. 6. Influence of nearby industrial and traffic sources on the concentrations of  $\Sigma$ Heavy-PAHs. Indoor air—filled circles and solid line; Outdoor air—open circles and dashed line.

both the mean and the median outdoor concentrations of  $\Sigma$ Light-PAHs were similar at the two homes. However, the indoor median at Home 10 is about four times higher than that of Home 09. At Home 09, the median I/O value of  $\Sigma$ Light-PAHs is 0.12, which is the lowest among the 10 homes. By comparison, the median I/O of  $\Sigma$ Light-PAHs is 1.3 at Home 10, the highest among the 10 homes. In addition to the difference in house age (Home 10 is 80 years old, while Home 09 is only 8 years old), significant indoor sources may have existed at Home 10, including frequent baking and broiling of food. Other PAH-related indoor activities recorded at some homes during the study period include candle and incense uses, overcooking of food, indoor application of insect repellent, etc. Elevated levels of PAHs were observed for some of the events but not in other occurrences of the same type of event.

Prior to the start of sampling, each home was assigned a level of industrial pollution (low, medium, or high) based on potential PAH sources, both mobile and stationary, in the surrounding area. The rating for Home 06 was later changed from the initial “heavy” to “medium” after visiting the home, which, although within the boundaries of heavily industrialized Gary, Indiana, was located in a quiet neighborhood with low traffic volume, surrounded by similar small homes and lots of trees, and there were no major industries within a radius of 1.5 miles. Fig. 6 illustrates the strong dependence of the home medians of  $\Sigma$ Heavy-PAHs, especially those outdoors, on the assigned industrialization level. GLM analyses on  $\Sigma$ Heavy-PAHs using industrial pollution level as the single class variable resulted in  $p$ -values of 0.049 and 0.029 for the outdoor air and indoor air, respectively. Such significant dependence was not found for  $\Sigma$ Light-PAHs. Further statistical analysis using Duncan’s Multiple Range Test

on outdoor  $\Sigma$ Heavy-PAHs singled out Home 08 from other homes. Among the 10 participating homes, Home 08 had the highest mean and the highest 75% and 90% percentiles, although its median was not particularly high. This home was located at the corner bordering Midway Airport in Chicago, it is possible that dramatic, but likely short-term, increases in airborne heavy PAHs were brought about by airplanes take-off. Another aircraft related event occurred at Home 06, where low-flying airplanes from the annual Chicago Air & Water Show might be responsible for the significantly enhanced PAH levels both outdoors and indoors (with window open) on that day at this home. The influence of traffic and industries can also be seen at Home 05, located at the intersection of Interstate I-57 and a major road in the heavily industrialized Calumet area south of Chicago. Highest medians of both indoor and outdoor  $\Sigma$ Heavy-PAHs, as well as highest 75% and 90% percentiles for the indoor  $\Sigma$ Heavy-PAHs, were observed at this home. Sporadically occurring outdoor events, such as street paving and a neighborhood party with multiple food grills, were also found to increase the outdoor PAH levels above the home-specific 75–100% percentiles. In two cases of outdoor garbage burning, the 48-h averages of indoor concentrations were found to be more affected than those outdoors; higher dispersion rates outdoors may explain the observations.

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